Guidance on
Evaluation, Resolution, and Documentation
of Analytical Problems
Associated with Compliance Monitoring

Prepared by

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Foreword

This guidance document was prepared in response to questions directed to the Environmental Protection Agency (EPA) Headquarters by EPA Regions and various state agencies about monitoring compliance with the Organic Chemicals, Plastics, and Synthetic Fibers (OCPSF) Effluent Guideline Limitations promulgated by EPA in 1987. The Engineering and Analysis Division (EAD) in EPA's Office of Science and Technology within the Office of Water is responsible for promulgation of regulations controlling the discharge of pollutants into surface waters. EAD has developed analytical methods and collected and validated analytical data as part of the rulemaking process. To support compliance monitoring, EAD provides assistance to the EPA Regions and the States in evaluating claims of matrix interference problems associated with OCPSF and other proposed and promulgated regulations.

Recognizing that the guidance necessary to deal with these issues goes beyond the OCPSF Rule and beyond those Regions and States that have requested assistance, EAD has compiled this guidance under one cover for use by permit writers, permittees, laboratories, and other interested parties. This document is organized into six chapters:

- Data required to document matrix-related problems
- Guidance to analysts attempting to identify pollutants in OCPSF wastewaters
- Cost estimates for resolving matrix-related problems
- Guidance for review of data from EPA 600- and 1600-series methods for organic compounds
- Case histories of claims of matrix interferences
- Contracting for analytical services

This document addresses only those issues related to the analysis of organic compounds regulated under the OCPSF rule, but much of the approach can be applied to the analysis of other organics as well as to metals.

This document presumes knowledge of, or access to, the relevant analytical methods under discussion. The authors have found it necessary to sacrifice some level of detail in order to address as broad a range of situations as possible. Some analytical problems and some samples are not addressed in these pages. However, the approaches used to demonstrate the magnitude of problems with sample matrices can be applied to issues not specifically addressed here.

EPA's Engineering and Analysis Division is solely responsible for the content of this document. The document was prepared, in part, by DynCorp Viar Inc., under U.S. EPA Contract 68-D0-0083. Comments, suggestions, and requests for additional copies should be directed to:

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Chapter 1

Checklist of Laboratory Data Required to Support a Claim that the Permittee was Unable to Measure Pollutants Due to Matrix Problems

The Federal Water Pollution Control Act (FWPCA) Amendments of 1972, later amended as the Clean Water Act (CWA), require that all facilities that discharge wastewaters to the surface waters of the United States maintain a permit for such discharges under the National Pollutant Discharge Elimination System (NPDES). In addition, all such permitted dischargers (permittees) must monitor their effluent for compliance with any and all relevant federal and state discharge limitations.

CWA Section 304(h) requires EPA to promulgate test procedures appropriate for the measurement of regulated pollutants, commonly known as "the 304(h) methods." These methods are then published at 40 *CFR* Part 136. Test procedures may also be promulgated by EPA under the authority of other CWA sections, and these procedures are typically incorporated in revisions of 40 *C*FR Part 136. For some inorganic analytes and some organic pesticides, the test procedures promulgated under Section 304(h) include methods sponsored by organizations other than EPA, such as the American Society for Testing and Materials (ASTM) and the U.S. Geological Survey (USGS).

The permittee must use the 304(h) methods or methods promulgated in other regulations to demonstrate compliance with NPDES permit limitations. The 304(h) methods for non-pesticide organic compounds promulgated in 40 *CFR* Part 136 (49 *FR* 43234; October 26, 1984, and later corrections) are commonly referred to as the "600-series" and "1600-series" methods. This chapter addresses issues related to the analysis of organic compounds, but much of the general approach can be applied to the analysis of metals and other inorganics as well.

Table 1, at the end of this chapter, lists all of the 600- and 1600-series methods, indicating each method number, the general class of analytes to which each is applicable, the instrumentation required, and the regulatory status of each method (promulgated, proposed, or draft). These methods were designed to be applicable to a wide range of industrial effluents and were used to generate the data necessary for the development of each of the effluent guidelines promulgated by EPA. Despite this wide applicability, EPA recognizes that some sample matrices may fail to yield useful results when these analytical methods are employed. Therefore, EPA is prepared to consider claims that the effluent is compliant in those instances in which the effects of the sample matrix make measurements difficult or impossible. All such claims must be supported by specific analytical data; stating that "the sample could not be analyzed" is not acceptable documentation.

This chapter outlines the analytical data and other information required by EPA to evaluate a permittee's claim of compliance when complex matrices preclude measurement of the pollutants listed in the permit. The data required are identical to those gathered by EPA in developing the regulation.

Since different instrumentation provide different data (e.g., GC/MS procedures produce plots of mass intensities while GC procedures do not), the specific form of the data will differ according to the method. The following numbered items describe the data required to support a claim of compliance at a minimum.

1. The method number of the base method used for the measurement.

The methods required for NPDES compliance monitoring are specified in 40 *CFR* Part 136 (and elsewhere, as explained above). Although there are many similarities between the technical details of methods from other EPA programs and from other sources, it is not acceptable to use such other methods for NPDES monitoring in place of a 304(h) method. For instance, methods from the Office of Solid Waste SW-846 manual are not acceptable in instances where a 304(h) method exists, unless approved by the permitting authority in advance.

The 600- and 1600-series methods *do* provide flexibility to improve separations and reduce the costs of measurements, but method performance must not be sacrificed. The purpose of this flexibility is to allow for improvements in analytical technology, in part to address matrix effects. In order to invoke this flexibility, the analyst must start with one of the base 600- or 1600-series methods and improve upon it. Example improvements include the use of additional cleanup techniques, alternative gas chromatography or liquid chromatography columns, and more specific detectors.

Changing to an alternative method for the sake of convenience is contrary to the spirit of this flexibility. The change must be within the scope of the method used and must be for the sake of improvement, and this improvement must be supported by data demonstrating equivalent performance to that of the base method.

2. A detailed narrative discussing the problems with the analysis, corrective actions taken, and the changes made to the base method identified.

The permittee must also describe the reasons for the change to the base method, the supporting logic behind the technical approach to the change, and the result of the change.

Many compliance monitoring analyses are performed by contract laboratories on behalf of the permittee. However, the responsibility for providing the information to EPA rests with the permittee. The permittee must therefore impress upon its contract laboratories the need for detailed technical communication of problems encountered and solutions attempted. The narrative should be authored by an analytical chemist and written in terms that another analytical chemist can understand.

3. A summary level report or data reporting forms giving the pollutants for which analyses were conducted and the concentrations detected. For the pollutants that were not detected, the detection limits or estimated detection limits must be provided.

Such results must be provided for each field sample analyzed, including any dilutions and reanalyses.

If not specified in the base method, the means for estimating detection limits must be provided in the narrative. If the laboratory uses "flags" in its data reporting, the definition of each flag must be provided with the data.

4. A summary of all quality control results required by the base method.

These results include, but are not limited to, the following:

- Instrument tuning
- Calibration
- Calibration verification
- Initial precision and recovery
- Ongoing precision and recovery
- Matrix spike matrix spike duplicate results
- Surrogate recoveries
- Labeled compound recoveries (isotope dilution methods only)
- Blank results
- Quality control charts and limits

5. Raw data that will allow an independent reviewer to validate each determination and calculation performed by the laboratory.

This validation should consist of tracing the instrument output (peak height, area, or other signal intensity) to the final result reported. The raw data are method specific and may include any of the following:

- Sample numbers or other identifiers used by the both the permittee and the laboratory
- Extraction dates
- Analysis dates and times
- Sequence of analyses or run logs
- Sample volume
- Extract volume prior to each cleanup step
- Extract volume after each cleanup step
- Final extract volume prior to injection
- Digestion volume
- Titration volume
- Percent solids or percent moisture
- Dilution data, differentiating between dilution of a sample and dilution of an extract or digestate
- Instrument(s) and operating conditions
- GC and/or GC/MS operating conditions, including detailed information on
  - columns used for determination and confirmation (column length and diameter, stationary phase, solid support, film thickness, etc.)
  - analysis conditions (temperature programs, flow rates, etc.)
  - detectors (type, operating conditions, etc.)
- Chromatograms, ion current profiles, bar graph spectra, library search results
- Quantitation reports, data system outputs, and other data to link the raw data to the results reported. (Where these data are edited manually, explanations of why manual intervention was necessary must be included)
- Direct instrument readouts; i.e., strip charts, printer tapes, etc., and other data to support the final results
- Laboratory bench sheets and copies of all pertinent logbook pages for all sample preparation and cleanup steps, and for all other parts of the determination

The raw data required shall be provided not only for the analysis of samples, but also for all calibrations, verifications, blanks, matrix spikes and duplicates, and other QC analyses required by the base method. Data must be organized so that an analytical chemist can clearly understand how the analyses were performed.

6. Example calculations that will allow the data reviewer to determine how the laboratory used the raw data to arrive at the final results.

Useful examples include both detected compounds and undetected compounds. If the laboratory or the method employs a standardized reporting level for undetected compounds, this should be made clear in the example, as should adjustments for sample volume, dry weight (solids only), etc.

7. For GC/MS and other instruments involving data systems, the permittee should be prepared to submit raw data on magnetic tape or disk, upon request by EPA.

8. The names, titles, addresses, and telephone numbers of the analysts who performed the analyses and of the quality control officer who will verify the analyses.

If data are collected by a contract laboratory, it is the permittee's responsibility to see that all of the requirements in the methods are met by the contract laboratory and that all data listed above are provided. (See Chapter 6 for guidance on writing contracts for laboratory services.)

Table 1. 600- and 1660-Series Methods for Organics[1]

Method	Class of Analytes	Instrumentation	Status
601	Purgeable Halocarbons	GC/ELCD	Promulgated
602	Purgeable Aromatics	GC/PID	Promulgated
603	Acrolein and Acrylonitrile	GC/FID	Promulgated
604	Phenols	GC/FID, GC/ECD	Promulgated
604.1	Hexachlorophene and Dichlorophen	HPLC/UV	Draft
605	Benzidines	HPLC/Electrochemical	Promulgated
606	Phthalate Esters	GC/ECD	Promulgated
607	Nitrosamines	GC/NPD, ELCD	Promulgated

[1] Please note that other methods for the analysis of organic compounds are incorporated by reference in 40 *CFR* 136.

Table 1. 600- and 1660-Series Methods for Organics (cont.)

Method	Class of Analytes	Instrumentation	Status
608	Organochlorine Pesticides/PCBs	GC/ECD	Promulgated
609	Nitroaromatics and Isophorone	GC/FID, GC/ECD	Promulgated
610	Polynuclear Aromatic Hydrocarbons	HPLC/UV, Fluorescence	Promulgated
611	Haloethers	GC/ELCD/ECD	Promulgated
612	Chlorinated Hydrocarbons	GC/ECD	Promulgated
613	2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	Low Resolution GC/MS	Promulgated
614	Organophosphorus Pesticides	GC/FPD	Proposed
614.1	Organophosphorus Pesticides	GC/NPD	Proposed
615	Chlorinated Herbicides	GC/ECD	Proposed
616	C, H, and O Pesticides	GC/FID	Proposed
617	Organohalide Pesticides/PCBs	GC/ECD	Proposed
618	Chloropicrin and Ethylene Dibromide	GC/ECD	Proposed
619	Triazine Pesticides	GC/NPD	Proposed
620	Diphenylamine	GC/NPD	Proposed
621	Carbamate and Urea Pesticides	TLC	Draft
622	Organophosphorus Pesticides	GC/NPD	Proposed
624	Purgeable Organics	GC/MS	Promulgated
625	Base/Neutral and Acid Extractable Organics	GC/MS	Promulgated
626	Acrolein and Acrylonitrile	GC/FID	Draft
627	Dinitroaniline Pesticides	GC/ECD	Proposed
629	Cyanazine	HPLC/UV	Proposed
630	Dithiocarbamate Pesticides	UV/Vis, by CS_2 liberation	Proposed
630.1	Dithiocarbamate Pesticides	GC/Hall, by CS_2 liberation	Proposed
631	Benomyl and Carbendazim	HPLC/UV	Proposed
632	Carbamate and Urea Pesticides	HPLC/UV	Proposed
632.1	Napropamide, Propanil, and Vacor	HPLC/UV	Proposed
633	Organonitrogen Pesticides	GC/NPD	Proposed
633.1	Neutral Nitrogen-Containing Pesticides	GC/NPD	Proposed
634	Thiocarbamate pesticides	GC/NPD	Proposed
635	Rotenone	HPLC/UV	Proposed

Table 1. 600- and 1660-Series Methods for Organics (cont.)

Method	Class of Analytes	Instrumentation	Status
636	Bensulide	HPLC/UV	Proposed
637	MBTS and TCMTB	HPLC/UV	Proposed
638	Oryzalin	HPLC/UV	Proposed
639	Bendiocarb	HPLC/UV	Proposed
640	Mercaptobenzothiazole	HPLC	Proposed
641	Thiabendazole	HPLC/Fluorescence	Proposed
642	Biphenyl and Orthophenyl Phenol	HPLC/UV	Proposed
643	Bentazon	HPLC/UV	Proposed
644	Picloram	HPLC/UV	Proposed
645	Amine Pesticides	GC/NPD	Proposed
646	Dinitro Aromatic Pesticides	GC/ECD	Proposed
680	Organochlorine Pesticides/PCBs	GC/MS	Draft
1613	Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans	High Resolution GC/MS Isotope Dilution	Proposed
1618	Organochlorine Pesticides/PCBs, Organo-phosphorus Pesticides, and Phenoxy-Acid Herbicides	GC/ECD, GC/NPD	Draft[2]
1624	Volatile Organics	GC/MS Isotope Dilution	Promulgated
1625	Semivolatile Organics	GC/MS Isotope Dilution	Promulgated
1648	Organic Halides (OX) in Solids	Neutron Activation	Draft, 1/91
1649	Organic Halides (OX) in Solids	Combustion, Coulometric Titration	Draft, 1/91
1650	Adsorbable Organic Halides (AOX) in Wastewaters	Carbon Adsorption, Combustion, and Coulometric Titration	Draft, 1/91
1651	Total Oil and Diesel Oil in Drilling Muds	Retort, Gravimetric	Proposed

[2] Draft Method 1618 has been supplanted by Methods 1656, 1657, and 1658.

Table 1. 600- and 1660-Series Methods for Organics (cont.)

Method	Class of Analytes	Instrumentation	Status
1652	Oil and Grease by Solid-Phase Extraction	Solid-Phase Extraction, Gravimetric	Draft 12/91
1653	Chlorinated Phenolics in Wastewater	GC/MS Isotope Dilution	Draft, 12/91
1654	Diesel Oil in Drilling Muds	HPLC	Draft, 12/91
1656	Organohalide Pesticides	GC/ECD, GC/ELCD, GC/Microcoulometric	Proposed[2]
1657	Organophosphorus Pesticides	GC/FPD	Proposed[2]
1658	Phenoxy-Acid Herbicides	GC/ECD, GC/ELCD, GC/Microcoulometric	Proposed[2]
1659	Dazomet	GC/NPD	Proposed
1660	Pyrethrins and Pyrethroids	HPLC/UV	Proposed
1661	Bromoxynil	HPLC/UV	Proposed

[2] Draft Method 1618 has been supplanted by Methods 1656, 1657, and 1658.

To obtain copies of the 600-series methods, write or call:

Chemical Research Division
USEPA Environmental Monitoring Systems Laboratory
26 Martin Luther King Blvd.
Cincinnati, OH 45268
513-569-7325

To obtain copies of the 1600-series methods, write or call:

USEPA Sample Control Center (operated by Viar & Co.)
P. O. Box 1407
Alexandria, VA 22313
703-557-5040

Note: Some 1600-series methods listed as "draft" may not be available through the Sample Control Center.

Additional information on analytes, methods, and regulatory limits may be found in EMMI, the EPA Environmental Monitoring Methods Index, a computerized database linking 50 EPA regulatory lists, 2600 substances, and 926 analytical methods. For information on obtaining the EMMI system software, contact:

National Technical Information Service
5825 Port Royal Road
Springfield, VA 22161
703-487-4650

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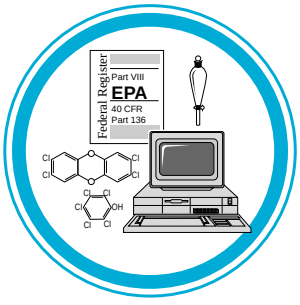

Chapter 2

Guidance for Analysts Attempting to Identify and Quantify Pollutants in Wastewaters Discharged from Plants Manufacturing Organic Chemicals, Plastics, and Synthetic Fibers

This chapter provides guidance to analytical chemists having difficulty in analyzing complex wastewaters from facilities that manufacture organic chemicals, plastics, and synthetic fibers. This guidance illustrates how the method equivalency and flexibility permitted by the wastewater methods can be used to apply other analytical techniques to matrix problems. This guidance specifically addresses the determination of the organic pollutants in these wastewaters. Conventional pollutants and metals are not addressed because few problems have been encountered in measuring these analytes in these wastewaters.

Table 2, at the end of this chapter, lists the organic priority pollutants regulated in wastewaters from organic chemicals, plastics, and synthetic fibers (OCPSF) industries and the EPA analytical methods relevant to monitoring such wastewaters.

Approved Methods for Determination of Organic Pollutants

Section 304(h) and other sections of the CWA authorize the EPA Administrator to promulgate test procedures for monitoring pollutants in wastewater discharges. Analytical methods (test procedures) to monitor organic priority pollutants in wastewater were proposed on December 3, 1979 (44 *FR* 69494) and promulgated in 40 *CFR* Part 136 on October 26, 1984 (49 *FR* 43234). These methods are variously known as the 304(h) methods, the 600-series methods, the 1600-series methods, and the Cincinnati methods. Additional methods have been proposed and/or promulgated under Section 304(h) since 1984. The 304(h) methods for organics are listed in Chapter 1, Table 1. Information on obtaining copies of these methods may be found at the end of that table.

The approved methods are based on recovery of organic pollutants from a wastewater sample by a purge-and-trap technique or by extraction with an organic solvent such as methylene chloride. In the purge-and-trap technique, the pollutants are purged from water with an inert gas and trapped on a sorbent column. The sorbent column is then heated and back-flushed to desorb the pollutants into a gas chromatograph (GC). The pollutants are separated by the GC and detected by a conventional detector (CD) or by a mass spectrometer (MS). Conventional detectors include the flame ionization detector (FID), electron capture detector (ECD), electrolytic conductivity detector (ELCD), and nitrogen-phosphorous detector (NPD).

Pollutants extracted from wastewater with an organic solvent are concentrated by evaporation of the solvent, and a portion of the concentrated extract is injected into a GC or high performance liquid chromatograph (HPLC), where the pollutants are separated and detected by a CD or MS. For application of GC and HPLC methods, EPA classified the organic pollutants into twelve groups of similar chemical and physical properties allowing each group to be measured under a given set of chromatographic conditions. Through the use of different detectors, several methods may be applicable to each of the twelve groups of pollutants. Table 3 lists the 304(h) methods applicable to

monitoring those pollutants specifically regulated under the OCPSF Rule, provides the general class of analytes to which the method is applicable, and specifies the applicable instrumentation.

Flexibility in Analytical Methods

In promulgating analytical methods for measurement of pollutants, EPA has provided flexibility for dealing with interferences. The major flexibility options are discussed in the preamble to the 40 *CFR* Part 136 methods (49 *FR* 43234). These options include a mechanism for obtaining approval of an alternative test procedure on a nationwide basis and/or on a site-specific basis (40 *CFR* Parts 136.4 and 136.5). These procedures are intended to encourage development of new analytical methods and to give analysts a number of options for resolving analytical problems that may be unique to specific wastewaters. If the discharger or an interested third party wishes to pursue the option of an alternative test procedure, that party should apply to the Director of the Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, for approval of an nationwide alternative procedure, or should apply to the State or Regional EPA permitting office for approval of a limited procedure.

In addition to the flexibility provided by the options above, flexibility is permitted in each analytical method. The analyst is permitted to "improve separations or lower the costs of analyses" provided that the results obtained are not less precise and accurate than the results obtained using the unmodified method. For example, the analyst is allowed to use professional judgment in selecting packed or open tubular columns, operating temperature programs, carrier gas or solvent flow rates, and detectors. Analysts may also use their discretion in selecting cleanup procedures and extract concentration procedures. The flexibility permitted is outlined in each method and in the preamble to the regulation.

EPA believes that method flexibility, which is discussed further below, should permit pollutant identities and concentrations to be determined in nearly all wastewaters, but recognizes that there may be a few intractable sample matrices that do not yield readily to extensive analytical efforts. EPA is anxious to learn of the steps taken by the analyst, the solutions found, and the instances in which a given matrix does not yield to known analytical techniques. Stating that "the sample couldn't be analyzed" is not sufficient and will not be accepted as justification for a claim of matrix interference.

Demonstrating Equivalency with a Given Method

The objective in modifying a method is to make it more specific for a given pollutant, more sensitive, more precise, more accurate, or in some other way to improve the method. However, some laboratories have interpreted the provision to modify a method as a means of increasing the speed of analysis, thus reducing the analysis time, or to take other "shortcuts" to reduce cost, resulting in a compromise of method performance. In regulating the wastewater methods, EPA needed a means to preclude this compromise in performance, yet permit the flexibility that would improve method performance.

EPA resolved this issue by providing limited flexibility within the methods, so that improvements could be made, and requiring the analyst to demonstrate that the results produced by any modification would be equal to or better than results obtained with the unmodified method. The yardsticks by which this performance is to be measured are precision and accuracy, but can be

extended to include detection limit, gas chromatographic resolution, mass spectral resolution, and other measures of method performance. The spirit of the regulation concerning methods is that method performance must be improved by any modification, and must not be degraded by such a modification.

The laboratory must perform a start-up test prior to practicing a method, and the results of the start-up test must be on record at the laboratory for inspection by EPA if desired. The start-up test provides an initial validation of the performance of the method by a specific laboratory. It is described in detail in Section 8 of the 600-series and 1600-series wastewater methods and is also used in the Office of Drinking Water 500-series methods and the Solid Waste SW-846 methods. The test consists of an analysis of four replicate volumes of reagent water spiked with the pollutants of interest at the concentration specified in the method or at 5–10 times the detection limit of the method.

For each analyte, the precision of the analysis of the four replicates, as determined by the standard deviation of the four measurements, must be less than the standard deviation specified in the method. Similarly, for each analyte, the accuracy of the analysis of the four replicates, as determined by the average percent recovery of the four measurements, must fall within the range of percent recovery specified in the method. If either the precision or accuracy test is failed, the test must be repeated until the laboratory is able to meet the precision and accuracy requirements.

If the laboratory modifies a method, the start-up test must be repeated with the modification as an integral part of the method. The laboratory must demonstrate that the precision and accuracy specifications in the method can be met with the modification; otherwise, the modification is not permitted. The laboratory must maintain records that document that the start-up test was performed on the modified method and that the precision and accuracy requirements were met.

Examples of Solutions to Matrix Problems

The inability to measure the concentration of a pollutant in a specific wastewater is often attributed to "matrix problems." Some example solutions to matrix problems are described below. The list is not exhaustive but should help the analyst to examine the specific matrix problems at hand and then to develop solutions to such problems.

Volatile Organic Pollutants

1. Use of selective GC detectors

   The 304(h) methods for volatiles include Methods 601, 602, 603, 624, and 1624. The effluent limits in the OCPSF regulation are all greater than 10 µg/L. The selective GC detectors in Methods 601 and 602 cover all OCPSF volatile pollutants regulated, and allow detection at levels well below the effluent limits in the OCPSF regulation. The specificity provided by the electrolytic conductivity detector and by the photoionization detector allow detection of the halogenated and aromatic analytes, respectively, in complex matrices.

2. Micro-extraction and gas chromatography with selective detectors

   The selective GC detectors in Methods 601 and 602 provide sensitivity that is 10–100 times greater than that required to detect the analytes of interest. Some of this sensitivity can

be used to substitute micro-extraction in place of purge-and-trap. The advantage of micro-extraction is that the pH of the water can be adjusted to attempt to keep the interferences in the water while the analytes of interest are extracted.[1]

3. Sample dilution

Methods 601 and 602 can achieve method detection limits of less than 1 µg/L for all volatile analytes in the OCPSF regulation, and of less than 0.1 µg/L for many of these analytes. The added sensitivity of the selective GC detectors can be used to overcome matrix problems by diluting the sample by a factor of 10–100. Even with this dilution, the pollutants can be detected at the levels required, and the effects of the interferences will be reduced or eliminated.

4. Isotope dilution

Method 1624 employs stable, isotopically labeled analogs of the pollutants as internal standards in the analysis. The use of these labeled compounds frequently permits the pollutant to be determined in the presence of interferences because the unique spectrum of the labeled compound can be located in the presence of these interferences, and the pollutant can then be located by reference to the labeled compound.

Semivolatile Organic Pollutants

1. Use of selective GC detectors

Methods 604 through 612 employ gas chromatography with selective detectors and high-performance liquid chromatography with an ultraviolet (UV) or electrochemical detector to detect pollutants in the presence of interferences. In addition, Method 604 employs derivatization and a halogen-specific detector for the determination of phenols. As with volatiles, the added sensitivity of the selective detectors permits the sample to be diluted by a factor of 10–100 while allowing detection of the analytes at the effluent limits specified in the OCPSF regulation.

2. pH change

A very powerful means of separating the pollutants of interest from interferences is to adjust the pH of the sample to keep the interferences in solution while allowing the pollutants to be extracted in an organic solvent. For example, neutral pollutants can be extracted at either low or high pH. Therefore, if the main interferences are acidic, the pH can be adjusted to >13 and the acidic interferences will remain in the water as their salts while the neutral pollutants are extracted using an organic solvent.

[1] Rhodes, J.W., and Nulton, C.P., *J. Env. Sci. and Health*, vol. A15, no. 5, (1980).

Phenol and 2,4-dimethylphenol can be extracted at high pH (11–13) using continuous liquid/liquid extractors, as described in Method 1625. This permits phenol and 2,4-dimethylphenol to be extracted in the presence of other, stronger acids.[2]

In a manner analogous to the pH change described above, the extract from the primary extraction can be back-extracted with water of the opposite pH to remove other interferences. To keep the organic pollutants in the extract, the water used for back-extraction can be saturated with salt (sodium sulfate and/or sodium chloride). Aqueous solutions containing 2% of each of these salts have been shown to be effective in keeping the pollutants of interest in the extract.

3. Gel-permeation (size-exclusion) chromatography

This technique is described in Revision C of Method 1625. The same technique is used in the Superfund Contract Laboratory Program (CLP) methods and SW-846 methods, and has been shown to be effective for removing lipids and high-molecular-weight interferences that can degrade GC and mass spectrometer performance.

4. Solid-phase extraction (SPE) cartridge

Although not fully evaluated at this time, SPE cleanup appears promising for not only neutral species but also for acidic and basic species. It has been shown to be effective in removing interferences from extracts containing pesticides and in the extraction of pollutants from drinking waters by Method 525. [3]

5. Florisil, alumina, and silica gel

These adsorbents are effective in separating neutral species from polar interferences. For polar analytes of interest, the adsorbent must be evaluated to determine if the analyte will be recovered. The level of activation of the adsorbent plays a major role in this recovery process.

6. Isotope dilution

Method 1625 permits determination of pollutants in the presence of interferences in semivolatile samples in the same way described for volatiles above. In addition, the wide range of recovery of the labeled analogs permitted in the method allows good quantitation of the pollutant when interferences reduce the efficiency of the extraction.

[2] Jackson, C.B. et. al., *J. Env. Sci. and Health*, vol. A15, no. 5, (1980).

[3] Tessari, J.D., *12th Annual EPA Conference on Analysis of Pollutants in the Environment*, Norfolk, Virginia, May 1989 (copies of the proceedings may be available through the EPA Sample Control Center, P. O. Box 1407, Alexandria, VA 22313, 703-557-5040).

Determination of Phenol as a Specific Example

Phenol is a commonly occurring pollutant in OCPSF wastewaters. The protocols below are suggested as approaches to the determination of phenol in a complex sample matrix. After a protocol has been found to be effective, the laboratory must demonstrate that the modification has equivalent performance to the original method. This demonstration involves the start-up tests described above. The specifications in the original method must be met before proceeding with analysis of a sample for compliance monitoring.

1. Base/neutral extraction, acid back extraction, and isotope dilution GC/MS (based on Method 1625)

    1.1 Measure 1.0 L of well-mixed sample into a graduated cylinder and spike with labeled phenol per Section 10 of Method 1625. Stir and equilibrate per this method. Quantitatively transfer the sample to a continuous liquid/liquid extractor. Adjust the pH of the sample to 11–13 and extract with methylene chloride as described in the method.

    1.2 Remove the extract from the extractor and place in a 1–2 L separatory funnel. Back-extract the extract sequentially three times with 500-mL portions of salt-saturated reagent water (pH <2), discarding the reagent water after each back-extraction.

    1.3 Concentrate the extract to 10 mL and clean up using gel-permeation chromatography (GPC) per Section 10 of Method 1625.

    1.4 After GPC, concentrate the extract to 0.5 mL and analyze by isotope dilution GC/MS, as described in Method 1625.

    1.5 Calculate the recovery of labeled phenol and compare to the performance specifications in Method 1625.

2. Dilution, acid extraction, back-extraction with base, derivatization, silica gel cleanup, and gas chromatography with an electrolytic conductivity detector (based on Method 604)

    2.1 Measure two 100-mL aliquots of well-mixed sample into 1000-mL graduated cylinders. Spike one of the aliquots with phenol at the level specified in Section 8 of Method 604. This aliquot serves as the matrix spike sample specified in the method. Dilute both aliquots to 1.0 L with reagent water. Adjust the pH of each aliquot to less than 2 with HCl.

    2.2 Pour each aliquot into a separate 1–2 L separatory funnel and sequentially extract three times with methylene chloride per Method 604. Discard the aqueous phase and return the extract to the separatory funnel.

    2.3 Back-extract the extract sequentially three times with salt-saturated reagent water, discarding the reagent water after each back extraction.

    2.4 Concentrate, derivatize, and clean up the extract per Method 604.

2.5 Analyze using the electrolytic conductivity detector. This detector is less susceptible to interferences than the electron capture detector used in Method 604. Newer models have sensitivity nearly equivalent to the electron capture detector.

2.6 Calculate the recovery of phenol in the matrix spike aliquot and compare this recovery to the specifications in Method 604.

Table 2. Priority Pollutants Regulated under the OCPSF Rule

Priority Pollutant	Applicable 304(h) Methods	Priority Pollutant	Applicable 304(h) Methods
Acenaphthene	610, 625, 1625	Methylene chloride	601, 624, 1624
Acrylonitrile	603, 624, 1624	Chloromethane	601, 624, 1624
Benzene	602, 624, 1624	Hexachlorobutadiene	612, 625, 1625
Carbon tetrachloride	601, 624, 1624	Naphthalene	610, 625, 1625
Chlorobenzene	602, 625, 1625	Nitrobenzene	609, 625, 1625
1,2,4-Trichlorobenzene	612, 625, 1625	2-Nitrophenol	604, 625, 1625
Hexachlorobenzene	612, 625, 1625	4-Nitrophenol	604, 625, 1625
1,2-Dichloroethane	601, 624, 1624	2,4-Dinitrophenol	604, 625, 1625
1,1,1-Trichloroethane	601, 624, 1624	2-Methyl-4,6-Dinitrophenol	604, 625, 1625
Hexachloroethane	612. 625, 1625	Phenol	604, 625, 1625
1,1-Dichloroethane	601, 624, 1624	Bis(2-ethylhexyl)phthalate	606, 625, 1625
1,1,2-Trichloroethane	601, 624, 1624	Di-*n*-butyl phthalate	606, 625, 1625
Chloroethane	601, 624, 1624	Diethyl phthalate	606, 625, 1625
Chloroform	601, 624, 1624	Dimethyl phthalate	606, 625, 1625
2-Chlorophenol	604, 625, 1625	Benzo(a)anthracene	610, 625, 1625
1,2-Dichlorobenzene	601, 602, 612, 624, 625, 1625	Benzo(a)pyrene	610, 625, 1625
1,3-Dichlorobenzene	601, 602, 612, 624, 625, 1625	3,4-Benzofluoranthene	610, 625, 1625
1,4-Dichlorobenzene	601, 602, 612, 624, 625, 1625	Benzo(k)fluoranthene	610, 625, 1625
1,1-Dichloroethylene	601, 624, 1624	Chrysene	610, 625, 1625
1,2-trans-Dichloroethylene	601, 624, 1624	Acenaphthylene	610, 625, 1625
2,4-Dichlorophenol	604, 625, 1625	Anthracene	610, 625, 1625
1,2-Dichloropropane	601, 624, 1624	Fluorene	610, 625, 1625
1,3-Dichloropropylene	601, 624, 1624	Phenanthrene	610, 625, 1625
2,4-Dimethylphenol	604, 625, 1625	Pyrene	610, 625, 1625
2,4-Dinitrotoluene	609, 625, 1625	Tetrachloroethylene	601, 624, 1624
2,6-Dinitrotoluene	609, 625, 1625	Toluene	602, 624, 1624
Ethylbenzene	602, 624, 1624	Trichloroethylene	601, 624, 1624
Fluoranthene	610, 625, 1625	Vinyl chloride	601, 624, 1624

Table 3. 304(h) Methods for OCPSF Organics

Method	Class of Analytes	Instrumentation
601	Purgeable Halocarbons	GC/ELCD
602	Purgeable Aromatics	GC/PID
603	Acrolein and Acrylonitrile	GC/FID
604	Phenols	GC/FID, GC/ECD
606	Phthalate Esters	GC/ECD
609	Nitroaromatics and Isophorone	GC/FID, GC/ECD
610	Polynuclear Aromatic Hydrocarbons	GC/FID/HPLC/UV,Fluorescence
612	Chlorinated Hydrocarbons	GC/ECD
624	Purgeable Organics	GC/MS
625	Base/Neutral and Acid Extractable Organics	GC/MS
1624	Volatile Organics	GC/MS Isotope Dilution
1625	Semivolatile Organics	GC/MS Isotope Dilution

Chapter 3

Cost Estimates for Resolving Matrix Interferences

Most of the options for resolving matrix interferences are outlined in Chapter 2. The costs associated with such options vary from laboratory to laboratory, as do the costs of the basic analysis. However, EPA has provided some guidance in Table 4 on the likely added costs of the work required to overcome such matrix interferences. These estimates are based on EPA's experience in contracting for analytical services.

The costs are estimated for repetitive routine monitoring of a given waste stream. The estimates do not include the development costs involved in modifying a given method to overcome a complex matrix problem. The cost estimates also do not include the costs of validating the use of additional cleanup techniques through the "start-up" tests described in Chapter 2. The costs of method modifications cannot be estimated because each complex matrix problem must be evaluated individually. EPA believes that these development costs could range between several hundred and several thousand dollars, depending on the complexity of the wastewater and the experience of the laboratory in resolving matrix interferences.

Given these difficulties, EPA believes that the prudent course is to begin by applying the cleanups and other techniques described in Chapter 2 to the existing 304(h) methods before embarking on a major modification of a method. The cost estimates in Table 4 are based on EPA's experience through 1992 and are given in round numbers.

Table 4. Estimated Incremental Costs Associated with Cleanup Techniques and Other Approaches to Resolving Matrix Interferences[1]

	Interference-reducing technique	Estimated incremental cost
VOLATILES	Use of GC with selective detector in place of GC/MS	No increased cost: should be less expensive than GC/MS
	Micro-extraction after pH adjustment	$25
	Sample dilution	No charge if known prior to analysis of neat sample, otherwise may be billable as another analysis
	Isotope dilution GC/MS (Method 1624)	$200 to $500
SEMIVOLATILES	Use of GC with selective detector in place of GC/MS	No increased cost: should be less expensive than GC/MS
	pH change	No charge
	Back-extraction	$25
	Gel permeation cleanup	$100
	Solid phase extraction cleanup	$100
	Florisil column cleanup	$25
	Alumina column cleanup	$25
	Silica gel column cleanup	$25
	Sample dilution	No charge if known prior to analysis of neat sample, otherwise may be billable as another analysis
	Isotope dilution GC/MS (Method 1625)	$200 to $500

[1] The techniques listed in this table are discussed in Chapter 2.

Chapter 4

Guidance for Reviewing Data from the Analysis of Organic Compounds Using EPA 600- and 1600-Series Methods

This chapter provides guidance for reviewing data submitted for compliance monitoring purposes under the National Pollutant Discharge Elimination System (NPDES) and data submitted to EPA and State authorities under the Clean Water Act. This guidance is intended to aid in review of data for organic compounds regulated under the OCPSF Rule and collected using the 600-series and 1600-series wastewater methods under 40 *CFR* Part 136 (49 *FR* 43234). The principles of data review described herein are also applicable to data from the 500-series methods and the SW-846 methods.

The guidance is technically detailed and is intended for data reviewers familiar with the 600- and 1600-series methods and similar analytical methods. Reviewers unfamiliar with these methods should review the methods and the supporting background materials provided in the preamble to the regulation (49 *FR* 43234).

Standardized Quality Assurance/Quality Control

In developing methods for the determination of organic pollutants in wastewater, EPA sought scientific and technical advice from many sources, including EPA's Science Advisory Board, scientists at EPA's environmental research laboratories, scientists in industry and academia, and scientists, managers, and legal staff at EPA Headquarters. The result of discussions held among these groups was the standardized quality assurance and quality control (QA/QC) approach that is an integral part of the 600- and 1600-series methods. This QA/QC takes the form of performance specifications for each method and contains the following elements:

1. Purity and traceability of reference standards
2. Number of calibration points
3. Linearity of calibration
4. Calibration verification
5. Method detection limit (MDL) or minimum level
6. Initial precision and recovery
7. Analysis of blanks
8. Recovery of analyte spikes into the sample matrix *or*
   Recovery of labeled compound spikes into samples (Methods 1624 and 1625).
9. Statements of data quality for recovery of spikes of analytes or labeled compounds into samples
10. Ongoing precision and recovery (Methods 1624 and 1625)
11. Statements of data quality for the laboratory

In reviewing data submitted for compliance, the permit writer or other individual or organization has the authority and responsibility to assure that the test data submitted contain the elements listed above; otherwise, the data can be considered noncompliant.

Provision of QA/QC Data

Permittees and other organizations submitting test data under the CWA or other acts may use their own laboratories or contract the testing to laboratories that meet the requirements specified in the methods. The permit writer can require that the supporting QA/QC data described above be submitted with results or that it be on record at the permittee's facility or at the testing laboratory.

EPA strongly suggests that the supporting QA/QC data be submitted along with the analytical results, so that the quality of the data can be evaluated directly, and so that these supporting data are not lost between the time of submission of the analytical results and the time that the QA/QC data are required.

In many of its early analytical programs, EPA relied upon laboratories to maintain records of the QA/QC data. This practice was cumbersome for the laboratories, because many of the QA/QC data were common to the analytical results for a variety of clients. Retrieving these data from the laboratory to resolve questions of permit compliance was time-consuming for the permittee and the permit writer. More importantly, this practice occasionally resulted in unscrupulous laboratories failing to perform the necessary QA/QC testing, or performing the QA/QC testing "after the fact" to satisfy an audit or data submission request. In particular, many laboratories did not perform the initial precision and recovery test (the "start-up" test) prior to practice of the method and did not perform a spike of the analytes into the sample matrix to prove that the method would work on a particular sample. Therefore, while the data provided by those laboratories may have been valid, there was no way to prove their validity.

When collecting data for the development of a regulation, EPA requires that the supporting QA/QC data be provided along with the results for the sample analyses. If an individual or organization submits analytical results for inclusion into EPA's regulations, EPA similarly requires the submission of the QA/QC data. The sample results are evaluated relative to the QA/QC specifications in the method, and those results that pass the QA/QC requirements are included for consideration. EPA believes that provision of the QA/QC data at the time of submission of the analytical results is essential to the timely and effective evaluation of permit compliance issues.

Details of Data Review

The details of the data review process depend to a great extent upon the specific analytical methods being employed for compliance monitoring. Even for data from the same methods, there are probably as many specific approaches as there are reviewers. However, given the standardized QA/QC requirements of the 600- and 1600-series EPA methods, a number of basic concepts apply. The following sections provide the basic details for reviewing data submitted and provide some of EPA's rationale for the QA/QC tests.

1. Purity and Traceability of Reference Standards

The accuracy of any non-absolute empirical measurement is dependent on the reference for that measurement. In determining pollutants in water or other sample matrices, the analytical instrument and analytical process must be calibrated with a known reference mate-

rial. The 600- and 1600-series analytical methods, as well as other EPA methods, require that the standards used for calibration and other purposes be of known purity and traceable to a reliable reference source.

The ultimate source for reference materials is typically EPA or the National Institute for Standards and Technology (NIST, formerly NBS). Permittees and their supporting laboratories submitting analytical data must be able to prove traceability of the reference standards used in the analysis to EPA or NIST. The proof of this traceability is a written certification from the supplier of the standard.

Documentation of the purity and traceability of the standards need not be provided with every sample analysis. Rather, it should be maintained on file at the laboratory and provided on request. When analyses are conducted in a contract laboratory, such documentation ought to be provided to the permittee the first time that a laboratory is employed for specific analyses and then updated as needed.

2. Number of Calibration Points

The 600-series methods specify a minimum of three calibration points. The lowest of these points is required to be near the MDL. The highest is required to be near the upper linear range of the analytical system, and the third point is approximately midway between the two. Methods 1624 and 1625 require calibration at five specific concentrations for nearly all analytes, and three or four specific concentrations for the remaining analytes for which the methods are not as sensitive.

The lowest calibration point should never be greater than five times the MDL and should ideally be within three times the MDL. The results for the lowest calibration standard are the principal means by which to assure that measurements at levels near the MDL are reliable.

The flexibility in selecting the levels of the calibration points in the 600-series methods has led to a wide variety of calibration ranges as each laboratory may determine its own calibration range. Some laboratories establish a relatively narrow calibration range, for instance a five-fold increase in concentration, because it makes it simpler to meet the linearity specifications of the 600-series methods. Other laboratories choose wider calibration ranges in order to minimize the number of samples that have to be diluted and reanalyzed because the concentration of one or more analytes exceeds the calibration range.

The data reviewer must make certain that all measurements are within the calibration range of the instrument. Samples with analytes outside of the calibration range should have been diluted and reanalyzed. The diluted sample results need only apply to those analytes that were out of the calibration range in the initial analysis. In other words, it is acceptable to use data for different analytes from different levels of dilution within the same sample. Some flexibility may be exercised in acceptance of data that are only slightly above (<10%) the calibration range. Such data are generally acceptable as calculated.

If data from an analysis of the diluted sample are not provided, limited use can be made of the data that are above the calibration range (>10%). The response of the analytical instrument to concentrations of analytes will eventually level off at concentrations above the

calibration range. While it is not possible to specify at what concentration this will occur from the calibration data provided, it is generally safe to assume that the reported concentration above the calibrated range is a lower limit of the actual concentration. Therefore, if concentration above the calibration range is also above a regulatory limit, it is highly likely that the actual concentration would also be above that limit.

3. Linearity of Calibration

The relationship between the response of an analytical instrument to the concentration or amount of an analyte introduced into the instrument is referred to as the "calibration curve." An analytical instrument can be said to be calibrated in any instance in which an instrumental response can be related to a single concentration of an analyte. The response factor (GC/MS methods) or calibration factor (GC, HPLC methods) is the ratio of the response of the instrument to the concentration (or amount) of analyte introduced into the instrument.

While the shape of calibration curves can be modeled by quadratic equations or higher order mathematical functions, most analytical methods focus on a calibration range where the response is essentially a linear function of the concentration of the analyte. The advantage of the linear calibration is that the response factor or calibration factor represents the slope of the calibration curve and is relatively constant, simplifying the calculations and the interpretation of the data. Therefore, all the 600- and 1600-series methods specify some criterion for determining the linearity of the calibration curve. When this criterion is met, the calibration curve is sufficiently linear to permit the laboratory to use an average response factor or calibration factor, and it is assumed that the calibration curve is a straight line that passes through the zero/zero calibration point. Linearity is determined by calculating the relative standard deviation (RSD) of the response factor or calibration factor for each analyte and comparing this RSD to the limit specified in the method. If the RSD does not exceed the specification, linearity is assumed.

In the 600- and 1600-series methods, the linearity specification varies from method to method, depending on the quantitation technique. The typical limits on the RSD are as follows:

- 15% for the gas chromatography (GC) and high-performance liquid chromatography (HPLC) methods
- 35% for analytes determined by the internal standard technique in the gas chromatography/mass spectrometry (GC/MS) methods (624, 625, 1624, and 1625)
- 20% for analytes determined by isotope dilution in Methods 1624 and 1625

If the calibration is not linear, as determined by the RSD of the response factor or calibration factor, a calibration curve must be used. This means that a regression line or other mathematical function must be employed to relate the instrument response to the concentration. Properly maintained and operated lab instrumentation should have no difficulty in meeting linearity specifications for 600- and 1600-series methods.

For determination of nearly all of the organic analytes using the 600- and 1600-series methods, the calibration curves are linear over a concentration range of 20–100 times the nominal concentration, depending on the detector being employed. Whatever calibration range is used, the laboratory must provide the RSD results by which one can judge linearity, even in instances where the laboratory is using a calibration curve. In instances where the laboratory employs a curve rather than an average response factor or calibration, the data reviewer should review each calibration point to assure that the response increases as the concentration increases. If it does not, the instrument is not operating properly, or the calibration curve is out of the range of that instrument, and data are not considered valid.

4. Calibration Verification

Calibration verification involves the analysis of a single standard, typically in the middle of the calibration range, at the beginning of each analytical shift. The concentration of each analyte in this standard is determined using the initial calibration data and compared to specifications in the method. If the results are within the specifications, the laboratory is allowed to proceed with analysis without recalibrating and use the initial calibration data to quantify sample results.

Calibration verification, used in the 600- and 1600-series methods, differs in concept and practice from "continuing calibration," which is used in the CLP and SW-846 methods. In continuing calibration, a standard is analyzed and new response factors or calibration factors are calculated on the basis of that analysis. If the new factors are close to the average from the initial calibration, all subsequent sample analyses are conducted using the new response or calibration factors. The degree of "closeness" is generally measured as the percent difference between the old and new factors. The problem with continuing calibration is that it amounts to a daily single-point calibration. Information about the behavior of the instrument at concentrations above and below this single standard can only be inferred from the initial multiple-point calibration.

Specifications for calibration verification are generally given as either a range of concentrations or as a percentage difference from the test concentration. For the 600-series semivolatile GC and HPLC methods, the difference must be within ±15%. For Method 625, the difference must be within ±20%. For the GC and GC/MS methods for volatiles and for Method 1625, a range of concentrations is given for each analyte. These ranges are based on interlaboratory method validation studies.

If calibration cannot be verified, the laboratory may either recalibrate the instrument or prepare a fresh calibration standard and make a second attempt to verify calibration. If calibration cannot be verified with a fresh calibration standard, the instrument must be recalibrated. If calibration is not verified, subsequent data are considered to be invalid until the instrument is recalibrated.

5. Method Detection Limit or Minimum Level

The 600- and 1600-series methods do not require that laboratories determine the method detection limit (MDL) for each analyte (40 *CFR* Part 136, Appendix B). However, laboratories that wish to practice any method on a routine basis must prove that they can measure pollutants at the MDL or the detection limit specified in the method. Performance of an MDL study in accordance with this procedure is one means of demonstrating such proficiency.

The ability to identify and quantify compounds at the "minimum levels" specified in Methods 1624 and 1625 must be demonstrated prior to the practice of these methods. The minimum level for any compound is the concentration in a sample that is equivalent to the concentration of the lowest calibration standard in the initial calibration, assuming that all method-specified sample weights, volumes, and procedures are employed. Therefore, data from the initial calibration must be submitted in order to demonstrate that the required sensitivity has been achieved.

If the minimum level in Methods 1624 and 1625 have not been achieved (as exemplified by calibration data), data are considered to be invalid.

6. Initial Precision and Recovery

This test is required prior to the use of the method by the laboratory. It is sometimes termed the "start-up test." The laboratory must demonstrate that it can meet the specifications in the method for the recovery of analytes spiked into a reference matrix (reagent water). EPA's experience has been that laboratories that have difficulty passing the start-up test have such marginal performance that they will have difficulty in the routine practice of the method. Performing the start-up test "after the fact" is not acceptable and may not be used to validate data that have been considered invalid because the start-up test was not performed.

The test consists of spiking the analytes of interest into a set of four aliquots of reagent water and analyzing these four aliquots. The mean concentration and the standard deviation of the concentration are calculated for each analyte and compared to the specifications in each method. If the mean and standard deviation are within the limits, the laboratory can use the method to analyze field samples. For some methods, a repeat test is allowed because of the large number of analytes being tested simultaneously.

If there are no start-up test data, or if these data fail to meet the specifications in the method, all data produced by that laboratory using that method are not considered valid. As with the documentation of the purity of the standards, the start-up test data need not be submitted with each set of sample results, but should be submitted the first time a laboratory is employed for analyses, and updated as changes to the method necessitate (see below).

It is important to remember that if a change is made to a method, the start-up test must be repeated with the change as an integral part of the method. Such changes may involve alternative extraction, concentration, or cleanup processes, alternative GC columns, GC conditions, or detectors, or other steps designed to address a particular matrix problem. If the

start-up test is not repeated when these steps are modified or added, any data produced by the modified method are considered not valid.

7. Analysis of Blanks

Blanks are required to be analyzed on a routine basis, when any part of the analytical process has been changed, and when contamination of the laboratory is suspected. The 600- and 1600-series methods require that a blank be prepared and analyzed with each set of samples. The size of a "set" is usually limited to a maximum of 20 field samples. In practice this means that on each day that a laboratory prepares samples, they must also prepare a blank, even if fewer than 20 samples are prepared. The purpose of analyzing a blank with each set of samples is to determine the extent of possible contamination of the samples while in the laboratory. If the blank is handled by the same analysts in the same way as the samples and the blank shows no contamination, it is likely that the samples will not have been contaminated. Requiring a blank to be analyzed after the analytical process has been changed is consistent with requiring a repeat of the start-up test, because the change introduces a new possibility for contamination of samples through the use of the new procedures.

Contamination in the laboratory is a common problem, though there are many opinions on what constitutes contamination. In the 600- and 1600-series methods, *any* concentration of a compound above the detection limit or minimum level of the method in question is a potential cause for concern. In reality, it is not unusual to find low levels of common laboratory solvents, phthalates, and other ubiquitous compounds in laboratory blanks.

Controlling laboratory contamination is an important aspect of each laboratory's quality assurance plan. The laboratory should maintain records, typically in the form of control charts, of blank contaminants. These records should prompt corrective action by the laboratory, including reanalysis of any affected samples. Such control charts may be requested by the reviewer in evaluating sample results; however, they are not routinely submitted with sample data.

Unfortunately, by the time that data on contaminants are submitted, it is usually too late for corrective action. Therefore, the reviewer has several options in making use of the sample data. First, if a contaminant is present in a blank, but not present in a sample, then there is little need for concern about the sample result, though it may be useful to occasionally review the raw data for samples without the contaminant to ensure that the laboratory did not edit the results for this compound.

The second approach deals with instances where the blank contaminant is also reported in a sample. Some general guidance will help you determine the degree to which the contaminant is affecting sample results:

- If the sample contains the contaminant at levels of at least 10 times that in the blank, then the likely contribution to the sample from the contaminant in the laboratory environment is at most 10%. Since most of the methods in question are no more accurate than that level, the possible contamination is negligible.

- If the sample contains the contaminant at levels of at least 5 times but less than 10 times the blank result, the compound is probably present in the sample, but the numerical result should be considered an upper limit of the true concentration.

- If the sample contains the contaminant at levels below 5 times the level in the blank, there is no adequate means by which to judge whether or not the sample result is attributable to laboratory contamination. The results for that compound in that sample then become unacceptable for compliance monitoring.

There are two difficulties in evaluating sample results relative to blank contamination. First, the reviewer must be able to associate the samples with the correct blanks. For analysis of volatiles by purge-and-trap techniques, where no sample extraction is required, the blanks and samples are associated by analysis date and time, and specific to the instrument as well. For methods involving the extraction of organic compounds from the samples, the blanks and samples are primarily associated by the date on which they were extracted, and by the batch of samples and associated lab equipment (glassware, reagents, cleanup media).

The second difficulty involves samples that have been diluted. The dilution of the sample with reagent water or the dilution of the extract with solvent represents an additional potential source of contamination that will not be reflected in the results for the blank unless the blank was similarly diluted. Therefore, in applying the 10-times rule, the concentration of the sample is compared to the blank result multiplied by the dilution factor of the sample or sample extract. For instance, if 12 ppb of a contaminant are found in the blank, and the associated sample extract was diluted by a factor of 6 relative to the extract from the blank prior to analysis, then the sample result would have to be greater than 12×6×10, or 720 ppb, to be acceptable. Between 360 ppb and 720 ppb, the sample result would best be considered an upper limit of the actual concentration. Below 360 ppb, the sample result is not acceptable for compliance monitoring.

Many laboratories would have the reviewer believe that subtracting the concentration of the analyte in the blank from the concentration of the analyte in the sample is a reliable method of determining the true concentration of the analyte in the sample. Unfortunately, experience indicates that this practice is not reliable. The obvious problem occurs when the blank concentration is higher than that in the sample, and subtraction would yield a negative concentration value. Using the 10-times rule above provides a more appropriate means of evaluating the results and does not require that the reviewer alter the results reported by the laboratory.

8. Recovery of Analyte Spikes into the Sample Matrix *or* Recovery of Labeled Compound Spikes into Samples (Methods 1624 and 1625)

The non-isotope dilution methods require a spike of the analytes of interest into a second aliquot of the sample for analysis with the sample. The purpose of spiking the sample (often termed a "matrix spike") is to determine if the method is applicable to the sample in question. The majority of the 600- and 1600-series methods were developed for the analysis of effluent samples and may not be appropriate for in-process samples. While many of the

methods were tested using effluents from a wide variety of industries, samples from some sources may not yield acceptable results. It is therefore important to evaluate method performance in the sample matrix of interest.

If the recovery of the matrix spike is within the limits specified in the method, then the method is judged to be applicable to that sample matrix. If, however, the recovery of the spike is not within the recovery range specified, either the method does not work on the sample, or the sample preparation process is out of control.

If the method is not appropriate for the sample matrix, then changes to the method are required. Matrix spike results are necessary in evaluating the modified method. If the analytical process is out of control, the laboratory must take immediate corrective action before any more samples are analyzed.

To separate indications of method performance from those of laboratory performance, the laboratory should prepare and analyze a quality control check standard consisting of a spike of the analytes in reagent water. If the results for the quality control standard are not within the range specified, then the analytical system must be repaired and the sample and spiked sample analyses repeated. If the recovery of this spike is within the range specified, then the analytical process is judged to be in control. However, the results of the sample analysis cannot be accepted for regulatory compliance purposes because the matrix spike results indicate that the method is not applicable to the sample.

In evaluating matrix spike results, the data reviewer must verify the following:

a. The unspiked sample has been analyzed.
b. The spiked sample has been analyzed.
c. The recovery of the spike is within the range specified.
d. If the spike recovery is not within the range specified, a QC check standard has been analyzed.
e. If a QC check standard has been analyzed, the results are within the range specified.

For isotope dilution analyses, the evaluation of the data is simpler because isotopically labeled analogs of the pollutants are spiked into each sample, and because a QC check standard (termed the "ongoing precision and recovery standard," or OPR) is analyzed with each sample set.

If the recovery of the labeled compound spiked into the sample is not within the range specified in the method, and the results of analysis of the ongoing precision and recovery standard are within the respective limits, the sample results are considered invalid. When labeled-compound recoveries are outside of the method specifications, the problem may be related to the sample matrix. The isotope dilution methods specify that, in these instances, the sample must be diluted with reagent water and reanalyzed. If the labeled compound recoveries meet the method specifications after dilution of the sample, then the results are acceptable, although the sensitivity of the analysis will be decreased by the dilution.

Unfortunately, for some sample matrices, even dilution will not resolve the problem, and for other matrices, the loss of sensitivity will preclude the use of the results for determining compliance. In these instances, additional steps need to be taken to achieve acceptable

results. Guidance as to what steps may be taken when the results of matrix-spike or labeled-compound recoveries are not within the limits specified in the methods is provided in Chapter 2. This guidance consists of suggestions for more extensive extraction and cleanup procedures, for sample dilution, and for other measures that can be taken to overcome matrix problems.

Using either non-isotope dilution or isotope dilution techniques, in instances where matrix spike or labeled compound recoveries are not within the specifications, it may still be possible to use the sample results for compliance monitoring purposes. In particular, if (1) the recovery of the spiked compound is above the method specifications and (2) the compound is not detected in the sample analysis, it is unlikely that the compound is present in the sample. This is because the factors that caused the analysis to over-estimate the concentration in the spiked sample would not likely have resulted in an under-estimate in the unspiked sample. For samples in which the compound is detected but the matrix spike or labeled compound recovery is above the method specifications, the concentration reported in the unspiked sample is likely an upper limit of the true concentration.

9. Statements of Data Quality for Recovery of Spiked Analytes or Labeled Compounds in Samples

The 600- and 1600-series methods specify that after the analyses of five spiked samples, a statement of data quality is constructed for each analyte. The statement of data quality for each analyte is computed as the mean percent recovery plus and minus two times the standard deviation of percent recovery for each analyte. The statements of data quality should then be updated by the laboratory after each five to ten subsequent spiked sample analyses.

For non-isotope dilution results, the statement of data quality can be used to estimate the true value of a reported result and to construct confidence bounds around the result. For example, if the result reported for analysis of phenol is 25 µg/L, and the statement of data quality for phenol is 70% ±30% (i.e., the mean recovery is 70% and the standard deviation of the recovery is 15%), the true value for phenol will be in the range of 28–43 µg/L, with 95% confidence. This range is derived as follows:

$$\text{Lower limit} = [(25 \div 0.7) - (25 \times 0.3)] = [35.7 - 7.5] = 28\ \mu g/L$$
$$\text{Upper limit} = [(25 \div 0.7) + (25 \times 0.3)] = [35.7 + 7.5] = 43\ \mu g/L$$

Many laboratories do not provide the data quality statements with the sample results, in which case the data reviewer must determine if the data quality statements are being maintained for each analyte and may need to obtain the data. If necessary, the reviewer can construct the data quality statement from the individual data points.

Statements of data quality for isotope dilution methods are based on the recoveries of the labeled compounds. Using an isotope dilution method, the sample result has already been corrected for the recovery of the labeled analog of the compound. Therefore, for a reported result for phenol of 25 µg/L where the standard deviation of the labeled phenol recovery is

15%, the true value for phenol will be in the range of 17–32 µg/L, with 95% confidence, derived as follows:

$$\text{Lower limit} = [25 - (25 \times 0.3)] = 17 \text{ µg/L}$$
$$\text{Upper limit} = [25 + (25 \times 0.3)] = 32 \text{ µg/L}$$

The lack of a statement of data quality does not invalidate results but makes some compliance decisions more difficult. If statements of data quality are not being maintained by the laboratory, there may be increased concern about both specific sample results and the laboratory's overall quality assurance program.

10. Ongoing Precision and Recovery (Methods 1624 and 1625)

Methods 1624 and 1625 require that an "ongoing precision and recovery" (OPR) standard be analyzed with each sample set, and that the results of this standard meet the acceptance criteria in the method prior to the analysis of blanks and samples.

The data reviewer must determine if the ongoing precision and recovery standard has been run with each sample set and if all criteria have been met. If the standard was not run with a given set of samples, or if the criteria are not met, the results for that set of samples are considered not valid.

For volatiles analyses by Method 1624, the OPR analysis is associated with the samples on the basis of the analysis date and time and the specific GC/MS system. For semivolatile analyses by Method 1625, OPR results are associated with samples extracted at the same time as the OPR.

Because of the large number of compounds being tested simultaneously in the 600- and 1600-series methods, there is a small probability that the OPR analysis will occasionally fail to meet the specifications. While the laboratory is supposed to correct any problems and analyze another OPR aliquot, it may still be possible to utilize the data associated with an OPR aliquot that does not meet all of the method specifications.

For instance, if the concentration of a compound in the OPR is above the method specifications but that compound is not detected in an associated sample, then it is unlikely that the sample result is affected by the failure in the OPR. If the concentration in the OPR is below the method specifications but that compound is detected in an associated sample, then the sample result is likely a lower limit of the true concentration for that compound.

11. Statements of Data Quality for the Laboratory (Methods 1624 and 1625)

In addition to statements of data quality for results of analyses of the labeled compounds spiked into the samples, Methods 1624 and 1625 require that statements of data quality be constructed from the initial and ongoing precision and recovery data. The purpose of these statements is to assess laboratory performance in the practice of the method, as compared to the assessment of method performance made from the labeled compound results for the

samples. Ideally, the two statements of data quality would be the same. Any difference is attributable to either random error or sample matrix effects.

If the laboratory is practicing isotope dilution methods, the data reviewer should review the statements of data quality for the laboratory. If the laboratory does not make these statements available for the reviewer, they may be requested. If the laboratory still does not make them available, it does not necessarily invalidate any data, but indicates that the laboratory may not be following the method as written.

Chapter 5

Case Histories of Claims of Matrix Interferences Submitted Under the OCPSF Rule

Chapter 1 described the data that would be required to demonstrate that a matrix problem precluded the measurement of a pollutant regulated under a NPDES permit limitation. This chapter provides case histories of selected claims of matrix interference problems submitted by dischargers regulated under the OCPSF rule.

Since 1991, the Engineering and Analysis Division (EAD) of EPA has reviewed data provided by at least 15 dischargers regulated under the categorical pretreatment standards for the OCPSF industry. In each instance, the discharger claimed that the facility's wastewater could not be monitored for compliance with the pretreatment standards because of interferences. EAD was asked to review such claims of matrix interferences by either the Region or State with permitting authority for the facilities in question. The various guidance documents collected here under one cover are an offshoot of the efforts to review such claims.

EAD's review focused on each facility's alleged inability to determine the organic analytes in its wastewater because of interferences. This chapter presents 11 case histories of EAD's review of data submitted by dischargers claiming interference problems and provides further detail as to how these dischargers might resolve matrix interference problems. None of the dischargers nor any of the laboratories involved are identified in this document.

Prior to reviewing the data, each of the permitting authorities was provided with copies of the following draft guidance documents:

- Draft Checklist of Laboratory Data Required to Support a Claim that the Permittee was Unable to Measure Pollutants Due to Matrix Problems (the "Checklist," updated as Chapter 1 of this report)

- Draft Guidance for Analysts Attempting to Identify and Quantify Pollutants in Wastewaters Discharged from Plants Manufacturing Organic Chemicals, Plastics, and Synthetic Fibers (the "Guidance for Analysts," updated as Chapter 2 of this report)

- Draft Guidance for Permit Writers and Others Reviewing Data from the Analysis of Organic Compounds Determined using the 600- and 1600-series Methods (the "Guidance for Permit Writers," updated as Chapter 4 of this report)

It was EAD's intention that these draft documents be provided to the dischargers and in turn to their laboratories, as needed. However, the review revealed that the documents had either not been provided by the States and Regions or were not followed.

In general, EAD's review of the claims submitted by 11 dischargers revealed the following:

- In nearly all instances where data were submitted, the dischargers and/or their contract laboratories were using incorrect analytical methods or did not follow the procedures required in 40 *CFR* Part 136.

- In other instances, the dischargers and/or their contract laboratories did not submit data necessary to document that the methods were being followed.

- Finally, the dischargers and/or their contract laboratories did not submit documentation regarding the nature of interferences and the attempts (if any) to resolve these interferences.

Case Histories

Case #1: This discharger used a contract laboratory for its analytical work. Information submitted by the laboratory revealed inconsistencies with the stated analytical methods.

The discharger allowed the laboratory to either

(1) Use alternative methods to the 40 *CFR* Part 136 methods, or
(2) Modify Methods 624 and 625.

Alternative methods are allowed under 40 *CFR* Part 136.4 and 136.5 provided that the facility submits the alternative methods to EPA's Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, (EMSL-Ci) for approval. Otherwise, alternative methods are not allowed. EAD found no reference to alternate methods approved by EMSL-Ci.

If Methods 624 and 625 were modified under the spirit of the 40 *CFR* Part 136 rule, these modifications were not documented and equivalence was not demonstrated. Modifications that the laboratory made to Methods 624 and 625 included:

- Combining acid and base/neutral fractions,
- Using a fused-silica capillary column for the analysis of acid and base/neutral fractions,
- Using alternative internal standards,
- Using alternative surrogates,
- Using higher detection limits,
- Using fewer matrix spike compounds, and
- Using matrix spike amounts inconsistent with regulatory compliance, background, or method-specified levels.

The preamble to the 40 *CFR* Part 136 methods (49 *FR* 43234, October 26 1984) states that a method is considered to be equivalent if its performance has been demonstrated to meet or exceed the specifications in the original method. None of the submitted data provided any evidence supporting method equivalence.

EPA recognizes that the use of multiple internal standards and a fused-silica capillary column for the base/neutral/acid fraction represent improvements; however, EPA does not accept that combining fractions, higher detection limits, alternative matrix spike compounds, and matrix spike amounts inconsistent with background or regulatory compliance levels represents improvement. On the contrary, these changes degrade method performance and are therefore in violation of both the spirit and letter of the flexibility permitted in the 600- and 1600-series 40 *CFR* Part 136 organic methods.

Method 625 requires the analysis of separate acid and base/neutral fractions (40 *CFR* Part 136, Appendix A: Method 625, Sections 10 and 12 and Tables 4 and 5). Because combining these fractions can compound matrix interference problems, the acid and base/neutral fractions should not have been combined for these analyses.

The matrix spike compounds and spiking levels used by the laboratory appeared to have been from Office of Solid Waste (OSW) SW-846 methods or from Superfund Contract Laboratory Program (CLP) methods. The 600- and 1600-series wastewater methods require the matrix spike compounds to be the compounds regulated in the discharge (e.g., 40 *CFR* Part 136, Appendix A: Method 624, Section 8.3) and require that the spike levels be at

(1) The regulatory compliance level,
(2) 1–5 times the background level of the analyte in the sample, or
(3) The level specified in the method (e.g., Method 624, Section 8.3.1).

The compounds spiked were not those regulated and the spikes were not at the levels required.

The matrix spike was performed on a diluted sample. Had the matrix spike been performed as specified in Method 624 or 625 (e.g., Method 624, Section 8.4.3), the spike would likely have failed the specifications in the method and the associated sample result could not have been reported for regulatory compliance purposes. This should have triggered cleanup procedures, the use of alternative methods, or modification of Method 624 or 625 to improve method performance, as detailed in the draft "Guidance for Analysts."

The QC specifications for matrix spike recovery used by the laboratory were not the specifications given in Methods 624 and 625. The specifications in the wastewater methods (40 *CFR* Part 136, Appendix A: Method 624, Table 5; and Method 625, Table 6) must be used for compliance monitoring. While tighter specifications from a documented source may be acceptable if met, use of wider limits without documentation would never be acceptable.

The detection limits reported for semivolatiles were, for the most part, twice the minimum levels given in Method 1625 and were approximately 10–20 times the method detection limits (MDLs) given in Method 625. No explanation for the increased detection limits was given, nor could the limits be derived from the data provided.

The laboratory made no attempt to clean up the samples using pH change, gel permeation chromatography, or the other techniques in the 600- and 1600-series methods or the draft "Guidance for Analysts."

Case #2: Information provided with data submitted by this discharger was insufficient for a detailed review (as outlined in the "Checklist of Laboratory Data").

Despite the general lack of data, it appeared the discharger submitted samples to a contract laboratory for analyses by a GC/MS method which failed to produce useful results. The discharger and/or the laboratory attributed the problems to large concentrations of acetone in the discharge, though this problem could not be confirmed from the information provided. The analytical contractor proposed to the discharger that Methods 601 and 602 be used for the volatiles analysis in an attempt to overcome the interference problems. Because these methods are both more sensitive and more selective than a GC/MS method, the analytes regulated should be measurable in the presence of a large

concentration of acetone. The discharger ignored the laboratory's proposal and submitted a claim of matrix interferences. EPA believes that the approach proposed by the laboratory is workable and appropriate, and should have been attempted. If Methods 601 and 602 were used (as with any other methods used), the analytical laboratory must adhere to all method specifications.

Case #3: This discharger used several contract laboratories for analyses. The "reports" from these laboratories consisted of summary reporting forms showing detection limits that were 10–50 times greater than the MDLs in Methods 624 and 625.

There were no QC results, no details of how the analyses were performed, and no documentation of interference problems or steps taken to overcome interference problems, and therefore no proof that an interference existed. The laboratory may have chosen to dilute samples for convenience. The discharger and its laboratory must provide the data listed in the "Checklist of Laboratory Data" and attempt to solve purported interference problems using the techniques discussed in the "Guidance for Analysts."

Case #4: This discharger submitted a report from one contract laboratory that contained insufficient information for evaluation; and two letters from a second contract laboratory describing a problem with 4,6-dinitro-*o*-cresol.

The report provided by the first laboratory indicated no results for spikes of the OCPSF-regulated analytes into samples, no details of how the analyses were performed, what interference problems were encountered, or what steps were taken to overcome interference problems. In addition, it appeared that the contract laboratory combined acid and base/neutral extracts, thus exacerbating interference effects.

The letters from the second laboratory describing the problem with 4,6-dinitro-*o*-cresol asked for suggestions on how to determine this compound in the presence of interferences. The "Guidance for Analysts" provides general suggestions for overcoming matrix interference problems and specific suggestions for determination of phenol. The specific suggestions for determination of phenol can be applied to 4,6-dinitro-*o*-cresol.

Other reports by the contract laboratory showed high detection limits for the substituted phenols because of a huge quantity of phenol in the sample. One solution to this analytical problem is for the facility to reduce the level of phenol in the wastewater. The analytical laboratory should have used the procedures for determination of phenol detailed in the "Guidance for Analysts."

Case #5: This discharger submitted letters and reports from several contract laboratories. One report contained only some of the data required by the "Checklist of Laboratory Data."

Data items that were present and are required for a thorough review were instrument tunes, run chronologies, chromatograms, calibration data, calibration verification data, results for blanks, quantitation reports for samples, and matrix spike data run against the QC limits for Methods 624 and 625. The initial precision and recovery (IPR) data that demonstrate method equivalence were missing.

The semivolatile matrix spike data were inconsistent. The results of the unspiked samples indicated that some of the acids and base/neutrals were not detected, yet the results for the spiked samples showed large concentrations of some of these analytes that were not spiked into the samples.

The volatiles matrix spike had been diluted by a factor of 200 and spiked after dilution. Diluting and spiking will not show matrix interferences, and thus these data are of no value in evaluating the undiluted sample results.

Cases #6-#11: These facilities submitted summary reports from their laboratories.

None of the materials contained the information required by the "Checklist of Laboratory Data," and none contained explanations of the nature of the interferences found or descriptions of attempts to overcome these interferences. These facilities should follow the guidance provided by EPA and should report all data required by the "Checklist of Laboratory Data" and the "Guidance for Permit Writers."

Chapter 6

Guidance on Contracting For Analytical Services

Most businesses and government organizations have procedures and policies governing the purchase of services and supplies. They range from simply assigning responsibility to one individual ("Joe handles all that...") to the myriad of complex procedures set forth in the Federal Acquisition Regulations (FAR). Once established, these various procedures and policies may be applied relatively easily to purchases of office supplies, computers, and janitorial services. However, most organizations experience problems when they attempt to apply these procedures to the purchase of analytical services.

At the heart of these problems is the difficulty in defining the services that are required. The purpose of this chapter is to provide a basic framework with which to define the technical and contractual requirements associated with purchasing analytical services related to compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The procedures outlined here are presented as guidance and may need to be modified to meet the specific policies of an organization. The level of detail presented is not sufficient to meet all of the requirements of the FAR, but is a subset of the procedures used by several EPA offices and their contractors. The procedures may represent some degree of "overkill" for private organizations; however, it is simpler to delete the unneeded detail in those instances than to add it when it is required. The procedures are designed for procuring analytical services from commercial laboratories, but may also be applied to requests for services from in-house laboratories.

Requirements Analysis

Defining what services are required is often the most difficult step. The commercial environmental laboratory business has grown to be a multi-million-dollar-per-year enterprise serving the diverse needs of clients regulated under a variety of federal and state environmental statutes. Many laboratories have recognized the importance of customer service and employ staff who are trained to assist clients in defining the requirements. Other laboratories, large and small, rely solely on the client to define the specific requirements. Still another group of laboratories, albeit a small group, perform analyses with little regard to the client's actual needs. One of the problems that arises when the client's requirements are poorly defined is the use of inappropriate methods. As noted in Chapter 1, NPDES compliance monitoring requires that the 304(h) methods be used. It is not the laboratory's place to decide that a method from another source, even another EPA source, is "close enough."

The "five W's" of journalism ("who, what, when, where, and why," with "how" thrown in for good measure) are a first step in defining the requirements. **"Who"** is the name of the client, including a set of specific contact points. The laboratory needs to know the name of the person who will be taking and shipping the sample, in the event that there are shipping delays, broken samples, etc. The laboratory needs the name of a technical contact, if any, in the event that there are analytical questions

that need to be resolved. The laboratory also needs to know the name of the administrative contact who will handle issues of billing, payment, etc.

"**What**" is a description of the samples to be analyzed, including:

- Number of samples,
- Matrices (e.g., wastewater, sludge, solids, soils, etc.), and
- Analyses required (volatile organics, pesticides, etc.).

"What" may also include information on the required methodology, the reporting format, and the quality assurance/quality control (QA/QC) requirements. It may also include a specific description of the "product" to be delivered to the client. EPA recommends (Chapter 4) that the client receive a copy of *all* data, raw and summary, associated with the analyses.

"When" specifies the approximate date that the samples will be shipped to the laboratory, including the means of shipment (hand-delivered, picked up by the laboratory, overnight air freight, etc.), and the date when the results are required by the client. It should also specify the date by which the results are required. The "turnaround time" is the length of time, usually in calendar days, from the receipt of the sample at the laboratory until the results are to be received by the purchaser. The turnaround time is often a function of a reporting deadline under a permit. One can often save cost by giving the laboratory as much time as possible to provide the data. Sampling early in the month may mean that one has more time before the data must be reported to the permitting agency.

Obviously, **"where"** includes the name of the laboratory, but it is important to include the *street address* of the laboratory to which the samples will be shipped and the name of the person assigned to receive the samples. It is also important to include the name and address of the laboratory's administrative personnel handling billing and payment issues, as these may be different from the address where samples are shipped.

"Why" is often overlooked by people who *assume* that everyone understands the purpose of the analysis. Simply stating that "the analysis of X wastewater samples for NPDES compliance monitoring is required" can give a laboratory a wealth of information. Among other things, it should inform the laboratory that a 304(h) method is to be used; however, just to be certain, the method required is also specified elsewhere (see "how" below). In contrast, a statement about *"groundwater monitoring"* ought to lead the laboratory to inquire as to the purpose of the analysis, and hence what methods might be required, as 304(h) methods may not be appropriate. The type of analyses required can also be included, further clarifying the requirements.

The last requirement to be explicitly stated is **"how."** Although information about the analysis is included in "what" and "why," it helps to be specific, stating the method that is required or requested. It is also important to specify the quality assurance and quality control operations that will be performed in association with the sample analyses. While the EPA 600- and 1600-series methods specify the level of QA/QC to be performed, there are some methods from other sources (SW-846, ASTM, AOAC, etc.) that have been approved under Section 304(h) for some analytes, and these methods may not be as explicit regarding the QA/QC requirements. The laboratory also needs to know how the data are to be reported and how many copies of the report are required.

Identifying Laboratories and Soliciting Bids

Identifying qualified laboratories can be a time-consuming process. While many laboratories advertise in the Yellow Pages and in various directories of professional services, those advertisements may not tell you much about the laboratory's abilities to fulfill your specific analytical requirements. However, *any* list of laboratories is better than none. In addition, state and EPA Regional personnel may be able to give you a list of laboratories in your area or nationwide, depending on the type of analyses required. Such lists are *not* an endorsement of these laboratories, but are provided as a starting point.

If your procedures require that you obtain competitive bids for laboratory services, you will usually have to identify a minimum of three laboratories from which to solicit bids. If you are not *required* to obtain competitive bids, it may still be useful to occasionally compare prices from competing laboratories.

Determining that a laboratory is *qualified* to perform the analyses is also a somewhat daunting task. You can always take the laboratory director's word for their capabilities. However, you then have to evaluate the consequences of making a error in judgment. While EPA is currently exploring the idea of a national laboratory accreditation program, it is unlikely that such a program will be in place for several years. In the meantime, you can begin to identify qualified laboratories by sending them a list of your requirements, identified above. Ask them to provide information regarding their qualifications to perform such work (SOQ). Obviously, this needs to be done well in advance of your need for actual analytical services. The laboratory should be willing to discuss your specific needs with you, and demonstrate how they will meet those needs. While not normally required for NPDES compliance monitoring, it is not unheard of to perform an on-site inspection of a laboratory prior to using their services. It may also be worthwhile in some instances to send performance evaluation samples (samples of known composition) to a laboratory prior to utilizing them for routine analytical work. Performance evaluation samples for various organic and inorganic analytes are commercially available from several vendors. These vendors may also prepare custom samples that focus on the regulated pollutants at a specific facility.

Once you have identified a group of laboratories, you may solicit bids by simply sending them a request for a bid, including the detailed requirements identified above. One possible format for such solicitations is included with this report as an attachment. This is a generic version of a format that several EPA contractors have used for some time.

The NPDES compliance monitoring requirements for a given facility may only require the analysis of a small number of samples monthly or quarterly. While those analyses are very important to you (the discharger), they may not represent a significant source of revenue for a given laboratory. At some level, you are paying for all the quality control analyses associated with your small number of samples. As a result, you may pay higher prices per sample. One way to address the cost issue is to pursue a longer-term contracting arrangement. Determine how many analyses of what types you will need for the next year, and ask laboratories to bid on the entire package. To do this, you must be able to approximate the schedule on which these analyses are needed, but that is often driven by permit requirements. The advantages to you are (1) a lower price and (2) less time spent arranging for

bids. The advantages to the laboratory are (1) knowing that the work is coming and (2) spending less time getting business.

Writing a Contract

Before writing a contract for any kind of services, consult with the appropriate legal staff at your facility or firm. They will obviously know the ins and outs of contract law in your state. A well-written contract will include the "five W's" outlined above. It will also address your right to review the data as needed, the timeliness of payment to the laboratory, and your ultimate right to determine that the work does not meet the requirements established in the contract.

The required data turnaround and analytical holding time must be stated clearly in the contract. If analytical holding times are applicable, they are generally stated in the analytical method. However, delays in sampling and sample shipment may necessitate specification of a "contract" holding time that is based on the analytical holding time minus any time required for sample shipment. Unless you can guarantee that the sample will be delivered as soon as the laboratory opens in the morning, it is typical to specify that the day that the sample is received at the laboratory is "day zero," and the counting of "days" begins with the following day as "day 1."

In addition to stating the time that the laboratory has to generate and deliver the data, it may be useful to assign some specific consequences to the possibility of late delivery. One approach is to assess a penalty of some percentage of the analytical price per day of lateness. In the past, EPA has used values of 1–2% per day after the due date that the data were delivered.

Obviously, such penalties for lateness cannot be due to changes in the requirements made after the samples were sent, or the fact that the methods requested were not applicable to the samples. Many of the remedies to matrix problems discussed in Chapter 2 *cannot* be expected to be carried out in the original turnaround time assigned to the sample. However, once you have established that your samples can routinely be analyzed by the requested methods, lateness becomes an issue of laboratory management practices, not sample matrix.

From time to time, almost every laboratory will produce data that are of little use for the intended purpose (compliance monitoring in this instance). While well-run laboratories will contact you as soon as they identify the problem and work with you to make the best of a bad situation, you may still find yourself with no useful data and a deadline approaching.

A contract should stipulate that the laboratory will reanalyze samples at no cost to the client if the problems are due to laboratory error. It should also state that the client has the right to inspect the results, and if they do not meet the requirements in the contract, the client has the right to reject the data, returning them to the laboratory without payment. Rejection of data should be based on sound technical review of the results. It also obligates the client to make no use of those results without making some payment to the laboratory.

The contract should discuss in what instances dilutions of samples and reanalyses are considered billable by the purchaser. Again, a laboratory should be prepared to do the job right the first time and not bill for reanalyses required due to their errors. In contrast, some samples may need to be diluted and reanalyzed in order to bring the results within the demonstrated calibration range of the instrumentation. When this occurs, the laboratory ought to be paid for this effort. Such reanalyses

can be figured into the original price, inflating the per-sample price for all samples to account for the need to reanalyze some samples, or it can be broken out as a separate cost. Similarly, for analyses involving an extraction or digestion as well as an analysis, it may be useful to specify the price for the extraction step and the analysis separately, as a reanalysis may not require an additional extraction.

The contract is not a one-sided agreement, and as such, it must give specific rights and recourse to the laboratory as well. You may be asked to negotiate specific contract issues with the laboratory beforehand. The time involved in this process will obviously vary, and one of the benefits of contracting over longer time periods than the immediate need for one analysis is that these negotiations need only take place once for a large number of samples.

Combined with a careful analysis of the requirements, a well-written contract can minimize or eliminate many common problems in procuring analytical services. It should enable the client to obtain technically sound, legally defensible, and timely analytical data to meet a variety of compliance monitoring needs.

Attachment:
Example Analytical Services Request

The following is an example of a generic analytical services request form. Variations on this form have been used by several EPA offices and their contractors for many years. This form is intended to assist the client in identifying and specifying their analytical requirements, and to transmit this information to a potential supplier of analytical services in a consistent format.

Analytical Services Request

Client Name:

Point of Contact (name and telephone number):

Date of Request:

1. General description of analytical services requested:

2. Definition *and* number of samples involved (specify wastewater, groundwater, sludge, soil, etc.)

3. Purpose of analysis (NPDES, SDWA, RCRA compliance monitoring, etc.)

4. Estimated date(s) of sample collection:

5. Estimated date(s) and method of shipment:

6. Sampling/shipping contact (name and telephone number):

7. Holding times associated with analysis (specify number of days, or state "per method"):

8. Number of days after sample receipt that data are required:

9. Analytical method required (specify method number, source, and date, and attach copy where practical):

10. Special technical instructions (provide information on known problems, possible solutions, matrix effects, etc.):

11. Data reporting requirements (specify format of data, QA/QC reports, number of copies, etc.)

12. Sensitivity required (specify "per requested method," or list analyte names, CAS numbers, and quantitation limits required):

13. Quality control requirements (summarize QC operations specified in the referenced method, and any additional requirements):

14. Action required if QC limits exceeded (specify reanalysis, contacting client immediately, etc.):

15. Other (use additional sheets or attach supplementary information, as needed):